



# Micro-nano hierarchical porous titania modified with ZnO nanorods for biomedical applications

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## ABSTRACT

A porous titania structure with micro-isolated holes and grooves is prepared by micro-arc oxidation on titanium and ZnO nanorods are subsequently electrodeposited on the walls of the pores to produce a micro-nano hierarchical structure suitable for biomedical applications. The hydrophilic property of the structure depends on both the porous structure of the titania as well as morphology of the ZnO nanorods. By changing the fabrication parameters, the structure of the hierarchical structure can be adjusted in order to fine tune surface hydrophilic properties. The micro-nano hierarchical structure is suitable hard tissue replacement implants and other medical applications such as photodynamic therapy (PDT).

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## 1. Introduction

Artificial tooth roots, joints, and other hard tissue implants made of titanium and its alloys are widely used clinically. Modern medicine has a higher demand for titanium implants and the use of chemical or physical methods to modify the surface structures can endow the originally bioinert titanium implants to possess certain favorable osteoinductive or osteoconductive ability in order to promote the growth of new bones around the implants [1]. By designing and fabricating the proper surface structure on the implants, cell adhesion and related biological behavior can be effectively controlled and optimized [2–5]. Hence, the effects of biomaterial topography on cell behavior such as cell shape, movement, adhesion, differentiation, and mutual interactions have become hot research topics. In fact, cells can “sense” the nanostructured surface topology and small variations can result in large changes in the cell response impacting cell growth, gene expression, and differentiation [6], for instance, within a narrow range of nanotube diameter between 15 nm and 100 nm. Park et al. found that cells exhibited the largest response to 15 nm titania nanotubes but the response was less on 70 nm and 100 nm nanotubes [7,8]. When human mesenchymal stem cells [9] and osteoblasts [10] were co-cultured on titania nanotubes with a diameter of 30–100 nm, the 100 nm nanotubes showed the greatest osteogenic differentiation and cell adhesion increased with decreasing

nanotube diameter reaching a maximum at 30 nm. Recent studies have mainly focused on materials with a single nanostructure such as nanotubes [7–10], nano-columns [11], nanoarrays [12], nano-pits [13], nanopores [14], and nanogrooves [15], but surfaces with composite nanotopological structures with different morphologies can also impact the cell behavior significantly.

In this work, a micro-nano hierarchical surface structure is formed by depositing ZnO nanorods on the pore wall surface of porous titania by micro-arc oxidation (MAO) and electrodeposition. By changing the processing parameters, the surface structure and hydrophilic properties can be readily tuned and controlled. The micro-nano hierarchical structure has potential applications in hard tissue replacement, photodynamic therapy (PDT), and photocatalytic degradation of toxic liquid organic pollutants.

## 2. Experimental details

Micro-arc oxidation was employed to fabricate the porous titania with different pore structures. The pure titanium sheets were polished with metallographic sandpaper and ultrasonically cleaned with acetone, deionized water, and ethanol successively. The titanium sheets were chemically polished in a solution of HF, HNO<sub>3</sub>, and deionized water at a volume ratio 1:4:5, rinsed with deionized water, and dried.

A sodium carbonate electrolytic solution was used in micro-arc oxidation (MAO). 10 L of the electrolyte with 20 g/L sodium carbonate and 1 g/L potassium hydroxide were stirred at a constant temperature of 40 °C. The WHD-30 type micro-arc oxidation powder was

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used in MAO with the pretreated titanium sheets being the anode and stainless steel sink as the cathode. The samples were suspended in the electrolyte during MAO. The constant voltage mode with a forward voltage of 200 V–500 V, negative voltage of 0 V–100 V, pulse frequency of 50 Hz–1000 Hz, duty cycle of forward 10%–20% and negative 0%–10% was adopted and the oxidation time was 10 min–30 min. After MAO, the specimen was removed and washed with deionized water.

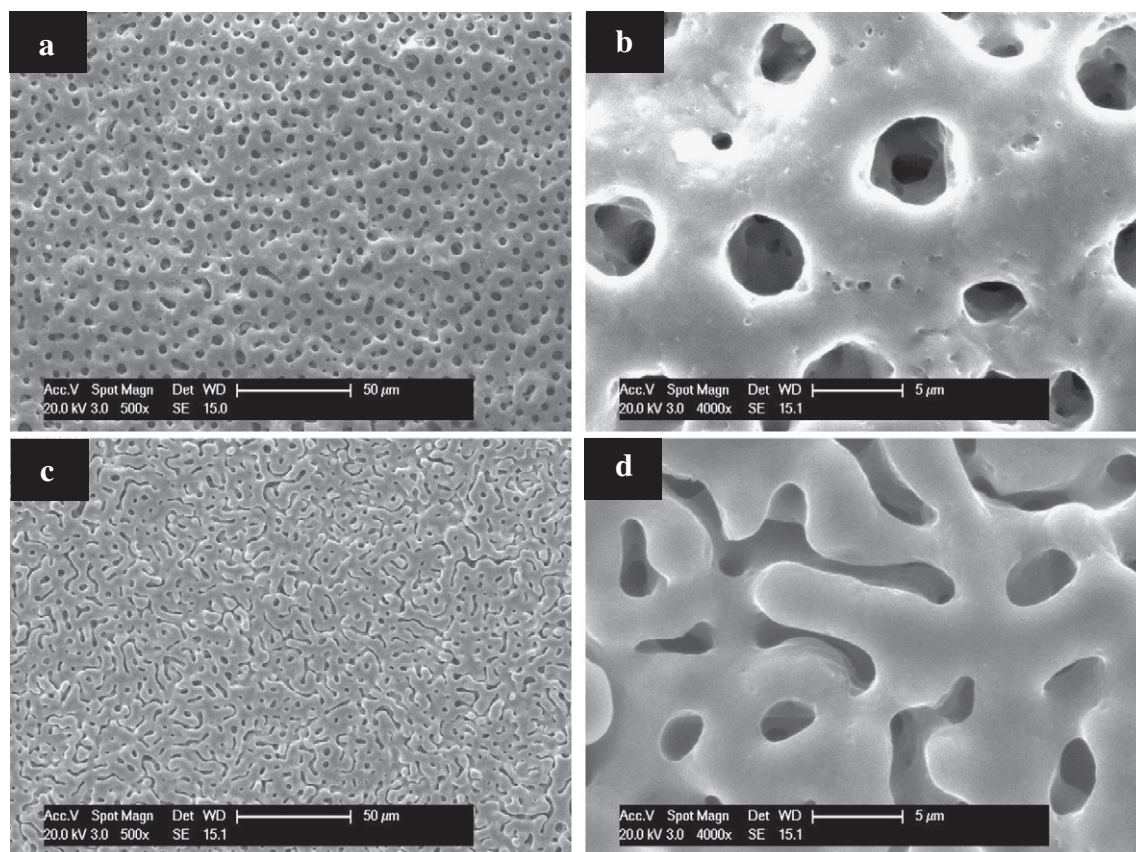
The pore wall surfaces of porous titania were deposited with ZnO nanorods by electrodeposition. The titanium sheets with porous titania surface were first washed with deionized water and dried. The electrodeposition electrolyte containing 1–5 mM  $Zn^{2+}$ , the same molar amount of hexamethylenetetramine (HMT), and 0.1 M–0.5M KCl was placed in a constant-temperature water bath at 60 °C–90 °C after purging with air for 2 h–10 h. The samples were placed in the bath as a cathode and the graphite electrode served as the anode. The electrodeposition time was 15 min–90 min and deposition voltage was 1.0 V–2.5 V. After that, the electrodeposited samples were ultrasonically washed with deionized water, and then dried.

An FEI SIRION field-emission scanning electron microscope (FE-SEM) was used to examine the morphology of the porous titania, ZnO nanorods, as well as micro-nano hierarchical structure at an accelerating voltage of 20 kV. The samples were coated with gold prior to SEM. A SHIMADZU XD-3A X-ray diffraction (XRD) instrument was used to determine the phases under the following conditions: Cu  $K_{\alpha}$  radiation, wavelength of 0.15406 nm, acceleration voltage of 40 kV, current of 30 mA, grazing angle of 2°, and scan range of 10°–90°. The measured angle error was less than  $\pm 0.01^{\circ}$ . The surface contact angles were determined using the liquid drop method on a contact angle goniometer (JC2000B, China). A 10  $\mu$ L droplet of deionized water was put onto the sample surface to measure the contact angle and each contact angle value was the average of 10 measurements.

### 3. Results and discussion

The porous titania with micro-isolated holes and grooves produced on titanium by MAO serves as the substrate for the micro-nano hierarchical surface structure. Fig. 1a and b depicts the morphology of the porous titania fabricated by MAO in the constant voltage mode using a voltage of 400 V and frequency of 50 Hz. The holes in the porous titania exhibit a uniform distribution and an isolated circular shape with a uniform diameter of approximately 5  $\mu$ m. Some small pores can be seen from the wall of the holes. Fig. 1c and d displays the morphology of the porous titania obtained under the same conditions except the MAO frequency which is increased to 800 Hz. The holes also exhibit a uniform distribution and a micro groove structure which can be attributed to the partial fusion of the micropores during the micro-arc discharge.

The formation of porous titania is discussed in the following. Initially, the titanium as the anode has good conductivity and the electrolyte contains a large number of ionic species. After the power is turned on, the anions aggregate onto the surface of the titanium plate under the external electric field and the titanium surface is oxidized to form a porous oxide film. At the same time, the non-conductive oxide film and physically-adsorbed gas on the porous anode surface can cause the partial-discharge effect. The microdischarge phenomenon occurs when the voltage is raised to a certain value. The discharge channel is formed in the interior of the film and then the micro-arc rapidly penetrates the oxide film. At a high MAO temperature, the oxide on the titanium surface and surface particles begin to melt. Partial melting softens the surface and finally, a porous structure is produced on the titanium surface. By increasing the MAO frequency while keeping the processing time and electrical parameters the same, more heat is generated near the electrodes causing a temperature rise in the electrolyte. This high temperature environment is not conducive to the



**Fig. 1.** Two porous titania with different porous structures fabricated by MAO on titanium surface: (a) micron isolated holes, low magnification; (b) micron isolated holes, high magnification; (c) micron grooves, low magnification; (d) micron grooves, high magnification.

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